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DETERMINATION OF SMALL QUANTITIES OF KRYPTON

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[Figures referred to are appended.]

The testing and systematic control of the operation of industrial krypton installations requires periodic determination of the content of krypton in a lean concentrate containing approximately 0.08 to 0.12% of the gas (cf. V. G. Fastovskiy, Krypton and Xenon, Gosenergoizdat, 1941).

This article will describe a method which the author has developed for determining small concentrations of krypton in a complex mixture of gases containing 99.7 to 99.8% oxygen and admixtures of hydrocarbons, nitrogen, argon, and carbon dioxide.

In solving the problem, a chemical method was selected for eliminating all accompanying chemically active gases with subsequent analysis of the residue containing krypton, argon, and nitrogen.

The residual gas may be analyzed by two methods: determination of the density of the argon-krypton mixture on a gas balance (cf. V. G. Fastovskiy and I. G. Gurvich, Zavodskaya Laboratoriya VIII, 1, 1939); or by measuring the pressure of saturated vapor of the mixture at the temperature of liquid oxygen.

Taking the gas sample in the customary 5- to 10-liter gasometer for subsequent analysis then requires precision work with extremely small quantities of inert gases since, with a one-percent krypton content in the lean concentrate, a 10-liter sample will contain no more than 8 to 10 ml of krypton and a small quantity of argon. Operations with such a quantity of gas are possible but impracticable.

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For this reason, it is more expedient to take a sample directly from the distillation vat of the first krypton column (Figure 1) through a buffer (1) and an accurately calibrated rheometer (2). In a period of 20-30 minutes, 50-100 liters of the concentrate may be drawn off and the oxygen eliminated by interaction with electrolytic hydrogen from a cylinder (3). The residue of the gas from the furnace (4) is partially freed of carbon dioxide in a vessel (5) which is filled with an alkali solution, and is then collected in a gasometer (6). The intensity of bubbling of the gas as it passes through the alkali solution in the vessel (5) may serve as an indicator of the furnace's operation. With strictly stoichiometric ratios of the flow of concentrate (rheometer 2) to that of hydrogen (rheometer 7), a slow current of gas bubbles through the solution of alkali is observed.

The quantity of gas in the gasometer, obtained from 50-100 liters of concentrate after combining of the oxygen, does not exceed 0.75-1.5 liters. The krypton content in this is already 7-10% or 50-150 ml, sufficient for analysis. Long practice has established that burning is completely safe and may be conducted expediently with a slight excess of oxygen.

The gas collected in the gasometer is then purified of hydrogen, oxygen, hydrocarbon impurities, carbon dioxide, and nitrogen, according to the stepwise process illustrated in Figure 2.

The gas is first passed into a vessel (1) which is submerged in another vessel (2) containing a mixture of liquid nitrogen and petroleum ether or absolute alcohol. Moisture and carbon dioxide freeze in this vessel at a temperature close to -100°.

Next, the gas passes via a valve (3) into a container (4) which has a 200 to 250-ml capacity and is filled with active (sponge) copper. This container is situated in a pipe furnace (5) with a temperature of 500-550°. With the valve (3) closed, the gas is transferred from the container (4) via another valve (6) into a small adsorber (7) which contains 7-8 g of activated carbon. With this valve (6) closed, the container (4) is refilled with gas from the gasometer (8). The operations are conducted two or three times to permit thorough purification of all the gas collected in the gasometer of oxygen and the stochiometric quantity of hydrogen, under static conditions. In the process all of the gas from the container (4) is transferred into the adsorber (7), and the entire system from the gasometer to valve (6) is completely evacuated.

The adsorber is submerged in a vessel (9) with liquid oxygen or nitrogen. While the valve (10) opens momentarily, desorbtion of the highly volatile components, i.e., hydrogen and nitrogen, is accomplished; then the vessel (9) is removed, the adsorber is heated to 150°, and the gas is transferred from the adsorber in a container (11) with pulverized calcium, and submerged in a furnace (12) where the temperature is held at 650-700°. A mercury vacuum pump (13) is used for complete evacuation of the gas from the adsorber and pipes. Combination of the main quantity of nitrogen takes place in a container (11). This operation is the longest and largely determines the total time required for the entire analysis.

From the container (11), the gas moves through a valve (14) into a condensation chamber (15) submerged in a vessel (16) which contains pure liquid oxygen. Complete evacuation of the container (11) is accomplished by means of a pump (13) which is used to transfer all the gas into the chamber (15).

A manometer (17) measures the pressure of the saturated vapors of the mixture of argon and krypton, and its composition is determined according to the equation:

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$$P = p^{o}_{Kr} \cdot x + p^{o}_{Ar} (1 - x),$$

wherein P is the total pressure determined from the manometer, and p^{o}_{Kr} and p^{o}_{Ar} are the saturated vapor pressures of pure krypton and argon at the temperature of liquid oxygen; x is the content of krypton in the mixture.

With a valve (18) open, the condensation chamber (15) is connected with a small cylinder (19) whose capacity is known; the chamber (15) is removed from the refrigerant and at room temperature pressure p_2 is calculated from an amnometer (17). The volume of the system, V_2, which includes the cylinder (19), chamber (15), and the connecting pipes from valves (18) and (20) to valves (21) and (10), must be determined beforehand. The total quantity of gas is determined by the formula:

$$V_3 = \frac{V_2 \cdot p_2}{760}$$

The quantity of krypton is calculated from the formula:

$$V_{Kr} = x \cdot \frac{p_2 \cdot V_2}{760}$$

and to determine the concentration of krypton in the original gas, the calculated value V_{Kr} is related to the total amount of concentrate processed in the furnace (4) (Figure 1).

By using a pump (13), the gas may be channeled from the cylinder (19) to the gas balance (22) to determine its density.

The balance readings may also be used to calculate the composition of the gas mixture. Agreement between the results of these two physical methods of analysis is sufficient confirmation of the accuracy of the results obtained.

With accurate assembly of the apparatus and some experience, analysis may be completed in 2 hours.

The entire apparatus must be evacuated beforehand with an oil pump to a residual pressure of the order of 10^{-2} mm Hg. The use of oil diffusion of mercury vacuum pumps is not necessary in this case. The apparatus, particularly the valves and pipe ends, must be tested for hermetic sealing.

The analysis proceeds in the following order. The entire system is evacuated and the vacuum maintained as the furnaces are being heated. The hydrogen is burned with the concentrate (Figure 1) and a minimum quantity of the gas, containing some excess of oxygen, is collected in the gasometer. The length of the combustion period and the readings of the rheometer (2) are accurately fixed. The vacuum apparatus is tested for hermetic sealing of manometers (23, 17) (Figure 2), after which the gas is purified of oxygen, hydrogen, and nitrogen with subsequent determination of the amount and composition of the residual gas.

The apparatus may be somewhat simplified and analysis considerably accelerated. To this end, the gas accumulated in the adsorber (7) is not transferred into the vessel (11) with pulverized calcium, but is passed through a valve (10) at a temperature of -110 to -115° C, and with the help of a vacuum pump, desorption of high volatile components is accomplished in 10-15 minutes.

The residual gas is moved from the adsorber when heated to 150° into a vessel (15) and then into a cylinder (19) for measurement of saturated vapor pressure and determination of gas volume. It is also well to determine its density.

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Such a method entails certain errors conditioned by the distilling-off, during desorption, of very small quantities of krypton, and also by the presence in the vessel of admixtures of nitrogen which alter the results of analysis during the measurement of saturated vapor pressure. However, it should be noted that even the adsorption of nitrogen admixtures by the pulverized calcium is not too effective.

For approximate analyses, which are adequate for regular operation of the krypton apparatus, all of the gas from the gasometer, after passing through the vessel for freezing out moisture and carbon dioxide, may be directed into the adsorber submerged in the vessel containing the refrigerant with a temperature of -110 to -120°; then, by a vacuum pump, in 10-15 minutes, desorption of the gas into the atmosphere may be accomplished. The remaining gas which, at the temperature of the cooling agent is not desorbed by the vacuum pump, is accumulated upon heating of the adsorbent to 150° in a cylinder whose volume is known. The last portions of the gas, used in determining its quantity, are evacuated by the pump and the gas then is moved to the balance for density measurement.

Since the density of nitrogen and oxygen is less than that of argon, a somewhat reduced value will be obtained for the krypton content. In addition, certain losses of krypton with the desorbed gas will lead to reduced analytical results.

If two or three parallel analyses, both exact and approximate, are conducted, the degree of error may be determined and, by adhering in all analyses to an unchanging system of combustion and desorbtion, a simpler apparatus minus furnaces and vessels with ground connections and having a minimum of vacuum valves may be used. The process of combining the nitrogen with metallic calcium may also be eliminated. The modified apparatus consists of a small asborber filled with 7-8 g of activated carbon, a cylinder of known volume, a manometer, a mercury vacuum pump, and a gas balance. The use of this apparatus considerably simplifies and shortens the time of analysis.

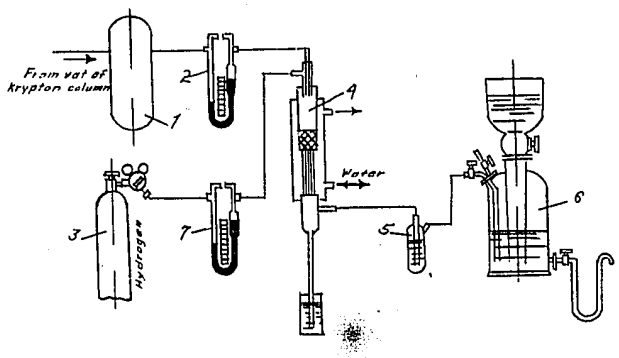

Figure 1. Diagram of Apparatus for Drawing Off Lean Concentrate From Distillation Vat of First Krypton Column and For Separation of the Main Quantity of Oxygen

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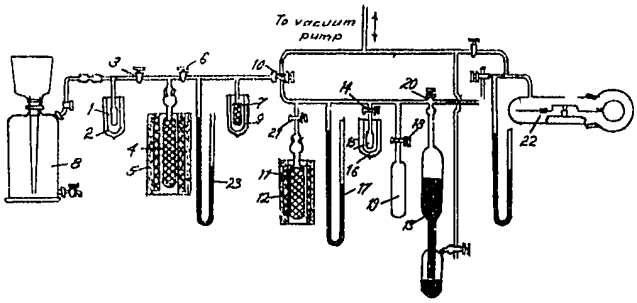

Figure 2. Diagram of Apparatus for Separation of Krypton From Gas Mixture

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